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XIII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON CERTAIN PRODUCTS OF THE DRY DISTILLATION OF WOOD: METHYLFURFUROL AND METHYLPYROMUCIC ACID.*

By Henry B. Hill and Walter L. Jennings.

Presented November 9, 1892.

Several years ago, one of us described † the occurrence of furfurol in not inconsiderable quantity among the products of the dry distillation of wood at low and carefully regulated temperatures, as carried on at Brooklyn under the direction of Dr. E. R. Squibb. Although attempts were made at the time to separate by fractional distillation the higher boiling constituents of the crude furfurol, ordinary boiling flasks alone were employed, and the results were so far from encouraging that a more thorough investigation was for the moment relinquished. The gradual accumulation of larger quantities of these higher-boiling oils encouraged us to renew the investigation, and we soon found that fractions of constant boiling point could readily be isolated by using in the distillation the extremely effective bead columns of Hempel.‡ The most noticeable fraction which we obtained was one boiling at 184–186°. This proved to contain chiefly methylfurfurol, a preliminary account of which was published § soon after its identification. A few months later Maquenne,‖ and Bieler and Tollens,¶ quite independently of each other, found the same methylfurfurol among the products formed by the distillation of several species of seaweed with dilute sulphuric acid, and showed that the fucusol of Stenhouse * was a mixture of furfurol with this methylfurfurol. Shortly afterward the same body was obtained by the action of dilute sulphuric acid upon isodulcite by Maquenne,† who pointed out that this mode of formation, taking into consideration the constitution of isodulcite as established by Fischer and Tafel,‡ proved the methyl group to be in the δ position. This conclusion of Maquenne concerning the structure of methylfurfurol was afterward confirmed in this Laboratory by a study of the product formed by the action of aqueous bromine upon methylpyromucic acid, and a brief description of this reaction was published at the time.§ Instead of the half-aldehyde of fumaric acid

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* A part of the work described in the following paper was presented in the form of a thesis to the Faculty of Arts and Sciences of Harvard University in May, 1892, by Walter L. Jennings, then candidate for the degree of Doctor of Philosophy.

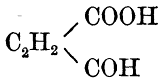
† These Proceedings, XVI. 155.

‡ Zeitschrift anal. Chem., XX. 502.

§ Berichte der deutsch. chem. Gesellsch., XXII. 607.

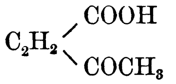
‖ Comptes Rendus, CIX. 571.

¶ Berichte der deutsch. chem. Gesellsch., XXII. 3062; Ann. Chem. u. Pharm., CCLVII. 110.



$$C_2H_2\Big\langle\begin{array}{l}COOH\\COH\end{array}$$

which is formed under like conditions from pyromucic acid, methylpyromucic acid yields the acetacrylic acid of Wolff,||



$$C_2H_2\Big\langle\begin{array}{l}COOH\\COCH_3\end{array}$$

and the formation of this ketone acid proves that the methyl group is attached to the δ carbon atom of the furfuran ring. We have also studied the action of dry bromine upon methylpyromucic acid, and have found that a somewhat unstable tetrabromide may be prepared, although the substitution products are more readily obtainable. For the preparation of the tetrabromide the temperature must be kept below 0°; if the bromine be allowed to act at ordinary temperatures a brommethylpyromucic acid is formed which melts at 150–151°, and contains the bromine in the furfuran ring, while at higher temperatures (50–60°) the bromine enters chiefly the side chain and forms ω-brommethylpyromucic acid melting at 147–148°. The formation of these two isomeric products at different temperatures recalls the analogous reactions in the aromatic series, and the analogy is completely borne out by the behavior

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* Ann. Chem. u. Pharm., LXXIV. 278.

† Comptes Rendus, CIX. 603.

‡ Berichte der deutsch. chem. Gesellsch., XX. 1092; XXI. 2173.

§ Ibid., XXIII. 452.

|| Ibid., XX. 426; Ann. Chem. u. Pharm., CCLIV. 245.

of the two acids. We have also made a dibrommethylpyromucic acid melting at 175°, in which one bromine atom is situated in the furfuran ring, the other in the side-chain. By the action of water upon the two acids which contain halogen in the side-chain we have made the corresponding oxy-acids.

We had intended to make a thorough study of the higher boiling fractions of the crude furfurol, and to determine as far as possible the nature of the various constituents; but the investigation of the methylfurfurol and its derivatives proved so much more attractive that we have contented ourselves with the partial examination of the fractions boiling at 200–215° and established in them the presence of guaiacol.

METHYLFURFUROL.

The material which we had at our disposal was that portion of the crude furfurol which remained behind at 175° on distilling the oil several times from ordinary retorts or boiling flasks. It had been accumulating for more than ten years, was dark in color, somewhat thick and viscous, and left on distillation a large tarry residue. We therefore distilled it from small copper retorts until signs of decomposition appeared. While the earlier investigations had shown that the temperature could be pushed to over 300° without essential decomposition, we now found that carbonization ensued at about 250°. At first we ascribed this difference in behavior to decomposition effected by long standing of the material; but we subsequently learned that changes had also been made in the mean time in the factory methods, and that it was quite possible that the greater part of our material had been subjected to the newer treatment. A special examination of the residue yielded by the distillation of nearly fifty kilograms of a fresh supply of crude furfurol showed that in this case decomposition also set in at 250°, so that no products boiling above this temperature could be obtained.

On fractioning with the aid of a Hempel column the yellow distillate which was first obtained, we soon found that it still contained considerable quantities of furfurol, and, aside from this, that a comparatively large portion distilled between 180° and 185°, and a smaller portion at 200–220°. As the distillation progressed, the intermediate fractions diminished in such a way that it became evident that but one body could be isolated between 165° and 200°, and that it boiled at a temperature not far from 185° (uncorrected). We therefore continued the distillation, taking two-degree fractions, and were able to collect a large portion which boiled with satisfactory constancy at 184–186°. As the material thus obtained showed the character of an aldehyde, a portion of it was shaken with a concentrated solution of acid sodic sulphite. The oil was almost wholly dissolved with the evolution of heat, and as the solution cooled it solidified with the separation of flat radiating prisms. These were drained thoroughly upon the pump, washed with cold alcohol, pressed, and dried. The dry crystals were then decomposed by the requisite amount of sodic carbonate in aqueous solution, and the liberated aldehyde distilled over with steam. The oil which passed over was then dried with fused calcic chloride and distilled. It showed the constant boiling point 187°, with the mercury column completely in vapor and under a pressure of 766 mm. The boiling point of a second preparation was found to be 186.5–187° under a pressure of 760 mm. An analysis of the oil showed that its formula was $C_6H_6O_2$.

0.1995 grm. substance gave 0.4788 grm. CO_2 and 0.0998 grm. H_2O.

	Calculated for $C_6H_6O_2$.	Found.
C	65.45	65.43
H	5.45	5.56

The formula of the substance, together with its strongly marked resemblance to furfurol, identified it as a methylfurfurol, and by oxidation with moist silver oxide it could readily be converted into the corresponding methylpyromucic acid.*

Freshly distilled methylfurfurol is a nearly colorless oil, with an odor closely resembling that of furfurol. On standing it grows dark-colored apparently more rapidly than furfurol, and acquires an acid reaction. The compound which it forms with acid sodic sulphite crystallizes in flat concentrically grouped prisms, which are usually rectangularly truncated. The salt dissolves in from two to three parts of water at ordinary temperatures. In the preliminary paper already referred to,† the statement was made that methylfurfurol gave the characteristic color reaction with a solution of rosaniline decolorized by sulphurous acid. We have found, however, that carefully purified methylfurfurol gives to this solution but a slight brown-red, or, if added in larger quantity, but a pale wine-red coloration, and are forced to conclude that the color formerly observed was due to a slight admixture of furfurol. It gives, however, with diazobenzol sulphonic acid when tested in the manner described by Penzoldt and Fischer * a color identical in shade with that given by furfurol. With hydrochloric acid and resorcine it gives an orange-red, with pyrogallol a carmine-red condensation product. Aniline acetate paper gives at first no color, or at best turns but a light yellow, but on standing a deep orange-color is developed. With phenylhydrazine a liquid hydrazone is formed, which we have not further examined. The specific gravity of methylfurfurol we have found to be somewhat higher than given by Maquenne.† A freshly prepared sample made with great care gave us at 18° referred to water at the same temperature the specific gravity 1.1087, or 1.1072 referred to water at 4°. As the sample was slightly colored it was distilled twice in a stream of hydrogen, but the specific gravity was altered but a few units in the fifth decimal place. The original fraction 186–187° (cor.) from which this sample was made gave a specific gravity of 1.1059. Maquenne found the specific gravity of his fraction 185–187° to be 1.107, and of the portion boiling at 187° to be 1.104. In water methylfurfurol is more sparingly soluble than furfurol, and requires about thirty times its weight of water at ordinary temperatures for complete solution.

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* See page 193.

† Berichte der deutsch. chem. Gesellsch., XXII. 607.

Since it was difficult to form even an approximate estimate of the relative amounts of furfurol and of methylfurfurol contained in the crude oil from an examination of the residues from previous distillations which we had at our disposal, we submitted to fractional distillation about 50 kilograms of the crude oil. We used a copper retort of eight litres' capacity, which was fitted with a suitable column made out of large thin-walled brass pipe and filled with glass beads. After repeated distillations we obtained about two per cent of the material taken in the fraction boiling from 182° to 186° (uncorrected), and sixty per cent in the fraction boiling from 160° to 165°. Although the absolute amounts doubtless would have been somewhat increased by further separation of the small intermediate fractions, the relative amounts could have been little altered.

Methylfurfuramide, $C_{18}H_{18}N_2O_3$.—An aqueous solution of methylfurfurol, when mixed with ammonic hydrate, gives after the lapse of some time a crystalline precipitate of methylfurfuramide. This substance crystallizes in slender radiating needles, dissolves readily in alcohol, ether, chloroform, benzol, or carbonic disulphide, but is more sparingly soluble in ligroin. The substance recrystallized from ligroin was found to melt at 86–87°, and contained the proper percentage of nitrogen.

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* Berichte der deutsch. chem. Gesellsch., XVI. 657.

† Ann. Chim. Phys., [6.], XXII. 84.

0.3510 grm. substance gave 27.8 c.c. of moist nitrogen at 22° and under a pressure of 759 mm.

	Calculated for $C_{18}H_{18}N_2O_3$.	Found.
N	9.03	8.96

GUAIACOL.

The larger fractions of the oil boiling above methylfurfurol were those which were collected between 200° and 220°, but even after long continued distillation no substances of constant boiling point could be isolated. While the oil did not appear to contain an aldehyde in sensible quantities, a large portion of it was soluble in aqueous alkalies, and we thought it advisable to take advantage of this fact in order to simplify our task. The fractions 200–215° were therefore united, shaken with a solution of sodic hydrate, and the aqueous emulsion distilled with steam as long as oil passed over. The alkaline solution was then acidified and again distilled with steam. The neutral oil when dried with calcic chloride distilled at 210–220°, and we have not yet examined it further. The oil which was soluble in the alkaline solution boiled between 200° and 205°, and the thermometer remained for a long time constant at 202°. The physical properties of this oil and the emerald-green color which ferric chloride developed in its alcoholic solution left no doubt in our minds that it was guaiacol, and we thought that it could possibly be most conveniently identified with precision by converting it into the tribromguaiacol of Tiemann and Koppe.* On adding bromine to an alcoholic solution according to their directions, however, we obtained an unsatisfactory product. The melting point, although somewhat higher than that given by Tiemann and Koppe (102°), was not sharp, and was little improved by repeated recrystallization. As the inherent disadvantages in adding bromine to an alcoholic solution were sufficiently obvious, we substituted glacial acetic acid for the alcohol, and at once obtained a definite product. From 5 grams of our oil we obtained 8.3 grams of a highly crystalline, nearly colorless bromine derivative, which melted at 111–112°, and a single recrystallization sufficed to raise the melting-point to 115–116°. Further recrystallization from alcohol or benzol failed to raise this melting-point. While our product thus melted 14° higher than the tribromguaiacol of Tiemann and Koppe, it agreed in other respects with their description, and the following analyses show that it had the same composition: —

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* Berichte der deutsch. chem. Gesellsch., XIV. 2017.

I. 0.2316 grm. substance gave 0.1974 grm. CO_2 and 0.0345 grm. H_2O.
II. 0.1603 grm. substance gave 0.2497 grm. AgBr.
III. 0.1705 grm. substance gave 0.2653 grm. AgBr.

	Calculated for $C_7H_5Br_3O_2$.	Found. I.	II.	III.
C	23.27	23.25		
H	1.39	1.65		
Br	66.48		66.30	66.24

Since we had failed to identify our substance as guaiacol through the melting point of this bromine derivative, we proceeded to prepare from it pyrocatechin. For this purpose we used, instead of the more usual hydriodic acid, hydrochloric acid, as W. H. Perkin, Jr.* had recently shown the decomposition was in this case nearly perfect if the reaction took place in sealed tube at 170–180°. On opening the tube, a gas escaped which burned with a green-bordered flame. The aqueous solution was extracted with ether, and the crystalline residue which was left upon evaporating the ether was distilled. The substance boiled at 240–242°, and the solidified distillate melted at 103–104°. When recrystallized from benzol it formed colorless lustrous scales, which appeared under the microscope to be rectangular plates, and melted sharply at 104°. The boiling point of pyrocatechin is usually given at 240–245°, and the melting point was found by Fittig and Mager † to be 104°. In aqueous solution our product also gave with ferric chloride an emerald-green coloration which turned to a violet-red on the addition of sodic carbonate. It was thus established with precision that pyrocatechin had been formed by heating with hydrochloric acid the oil under investigation, and the latter was therefore in its turn identified as guaiacol. It seems to us probable that the tribromguaiacol, which we have just described, is identical with that of Tiemann and Koppe, and that the low melting point which they observed was due to by-products introduced by their method of preparation. A more extended investigation of the matter was, however, wholly foreign to our line of work. We hope that the constituents of the crude furfurol which boil above 200° may be studied more fully in this Laboratory at some future time.

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* Journ. Chem. Soc., LVII. 589.

† Berichte der deutsch. chem. Gesellsch., VIII. 365.

METHYLPYROMUCIC ACID.

In order to prepare from methylfurfurol the corresponding methylpyromucic acid, we first attempted to follow the methods which we had already used in the manufacture of pyromucic acid from furfurol. We found, however, that alkaline hydrates, either in alcoholic or in aqueous solution,* gave us an extremely poor product in very unsatisfactory quantity. Although the experiments of Lessing in the laboratory of Limpricht † upon the oxidation of furfurol with argentic oxide, gave us little hope that we could in this way conveniently prepare large quantities of methylpyromucic acid, no better method suggested itself to us at the time, and we were forced to adopt it. To our surprise, we found that we could easily obtain in this way a weight of methylpyromucic acid which nearly equalled that of the aldehyde taken, and that we could also obtain from furfurol under the same conditions an equally satisfactory yield of pyromucic acid. From methylfurfurol we obtained as a maximum 84 per cent of the theoretical yield of methylpyromucic acid, from furfurol 82 per cent of the calculated amount of acid. As the weight of acid remaining in solution after precipitation with hydrochloric acid was in neither case taken into account, the reaction may fairly be called quantitative. The large yield which we obtained was doubtless due in part to a slight modification of the ordinary method of procedure, which we shall presently describe. Still we had no difficulty in obtaining from 10 grm. of furfurol in the usual way 8.5 grm. of argentic pyromucate, and from the acidified mother liquor by extraction with ether 2.9 grm. of pyromucic acid, so that the total yield of pyromucic acid in this case was 7.25 grm., or 62.1 per cent of the theoretical amount. All the methylpyromucic acid which we have used in our investigations we have made by the following method. 10 grm. of methylfurfurol were added to about 50 grm. of well washed argentic oxide suspended in about 800 c.c. of hot water, and the whole heated quickly to boiling. When the reaction appeared to be complete, pure sodic carbonate was added in quantity sufficient to precipitate the silver which had been carried into solution, and the feebly alkaline solution again boiled. When the fresh well marked reduction which then ensued was finished, the solution was filtered, evaporated to small volume, again filtered, and acidified with hydrochloric acid. The acid which separated as the solution cooled was nearly colorless, and as a rule a single recrystallization was sufficient to raise the melting point to the proper point. The slight color could be most conveniently removed, if necessary, by treating a solution of the calcium salt with bone-black.'

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* For many years a concentrated aqueous solution of sodic hydrate has been used at this Laboratory in the preparation of pyromucic acid. Our method has been, however, essentially different from that recommended by H. Schiff (Ann. der Chem. u. Pharm., CCXXXIX. 374, CCLXI. 254), in that we have destroyed the furfuryl alcohol by hydrochloric acid instead of removing it with ether. The saving of time and of ether has more than compensated us for the somewhat diminished yield. 2 litres of furfurol are very gradually mixed with 1200 c.c. of aqueous sodic hydrate (1 : 1), taking care by constant stirring and cooling that the thick paste does not grow hot. On the following day 2 litres of concentrated hydrochloric acid are gradually added, the temperature toward the end being allowed to rise somewhat to facilitate the complete decomposition of the furfuryl alcohol. If the temperature rises too rapidly, the reaction becomes violent. The furfuryl alcohol is in any case converted into a tough leathery substance, which grows brittle on standing with the excess of hydrochloric acid. The slightly colored mother liquor is drained off, the residue crushed in an iron mortar, 4 litres of water added, and then calcic hydrate, until the solution is permanently alkaline. After standing for several days, the solution being kept slightly alkaline, the pyromucic acid is carried completely into solution. The filtrate is but slightly colored, and this slight color may be almost wholly removed by bone-black. The yield of nearly colorless pyromucic acid which may be obtained in this way amounts to from 35 to 40 per cent of the weight of furfurol taken.

† Ann. Chem. u. Pharm., CLXV. 279. Lessing obtained a weight of pyromucic acid equal to but 14 per cent of the weight of furfurol employed, or but 12 per cent of the theoretical amount.

0.2067 grm. of the acid gave 0.4321 grm. CO_2 and 0.0900 grm. H_2O.

	Calculated for $C_6H_6O_3$.	Found.
C	57.14	57.01
H	4.76	4.84

Methylpyromucic acid melts at 108–109°, and sublimes readily at low temperatures. It is readily soluble in alcohol, ether, chloroform, or hot benzol, more sparingly soluble in cold benzol, and almost insoluble in carbonic disulphide. It is extremely soluble in hot water, and on cooling it separates from concentrated solutions in short, thick six-sided prisms, or in small six-sided plates formed by the development of these prisms parallel to the basal plane. From dilute solutions it frequently separates in feathery or bladed aggregations. The solubility of the acid in cold water we determined by titration with a standard solution of baric hydrate, using phenolphthalein as an indicator.

I. 22.293 grm. of a solution saturated at 20° required for neutralization 15.3 c.c. of a solution of baric hydrate, containing 0.01864 grm. BaO_2H_2 in 1 c.c.

II. 19.665 grm. of a solution saturated at 20° required for neutralization 13.55 c.c. of the above solution of baric hydrate.

According to these determinations an aqueous solution saturated at 20° contained the following percentages of acid: —

I.	II.
1.89	1.89

Methylpyromucic acid is therefore decidedly less soluble in water at ordinary temperatures than pyromucic acid.*

For the further characterization of the acid we have prepared a number of its salts.

Baric Methylpyromucate, $Ba(C_6H_5O_3)_2$. — This salt we made by boiling an aqueous solution of the acid with baric carbonate. The salt is readily soluble in cold water, somewhat less soluble in hot water, and separates on evaporation in small colorless octahedral crystals which are anhydrous. The salt thoroughly dried by pressure suffered no material loss of weight on exposure to the air.

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* According to Houton Labillardière (Ann. Chim. Phys., [2.], IX. 368), pyromucic acid is soluble in 26 parts of water at 15°. This result is confirmed by approximate determinations made in this Laboratory as a guide in the preparation of pyromucic acid. It was found that 100 c.c. of a solution saturated at 17° contained 3.35 grm. of the acid, and that 100 c.c. of a saturated solution of sodic chloride at the same temperature dissolved 0.60 grm. of the acid. The erroneous statement made in the preliminary description of the acid (Berichte der deutsch. chem. Gesellsch., XXII. 608), that it was "somewhat more readily soluble in water" than pyromucic acid, was based upon rough quantitative results obtained in recrystallizing from water the small quantity of the acid which I then had at my disposal. — H. B. H.

I. 0.3366 grm. air-dried salt gave 0.2023 grm. $BaSO_4$.
II. 0.4261 grm. air-dried salt gave 0.2562 grm. $BaSO_4$.

	Calculated for $Ba(C_6H_5O_3)_2$.	Found. I.	Found. II.
Ba	35.40	35.34	35.34

The solubility of the salt in water at ordinary temperatures we determined in the usual way.

I. 5.8353 grm. of a solution saturated at 19°.6 gave 0.7950 grm. $BaSO_4$.
II. 5.5326 grm. of a solution saturated at 19°.6 gave 0.7526 grm. $BaSO_4$.

According to these determinations the aqueous solution saturated at 19°.6 contained the following percentages of the salt:—

I.	II
22.62	22.59

In order to determine the solubility at higher temperatures we followed essentially the method recommended by V. Meyer.*

I. 6.8590 grm. of a solution saturated at 99° gave 0.8655 grm. $BaSO_4$.
II. 5.1805 grm. of a solution saturated at 99° gave 0.6480 grm. $BaSO_4$.

The aqueous solution saturated at 99° therefore contained the following percentages of the salt: —

I.	II.
20.95	20.78

Calcic Methylpyromucate, $Ca(C_6H_5O_3)_2 \cdot 2H_2O$. — The calcium salt is readily soluble in cold water, and the solubility is slightly increased by heat. It crystallizes in clusters of long radiating needles which contain two molecules of water.

I. 0.3544 grm. air-dried salt gave 0.1475 grm. $CaSO_4$.
II. 0.3184 grm. air-dried salt gave 0.1333 grm. $CaSO_4$.
III. 0.8481 grm. air-dried salt lost at 110° 0.0931 grm. H_2O.
IV. 0.5421 grm. air-dried salt lost at 110° 0.0596 grm. H_2O.

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* Berichte der deutsch. chem. Gesellsch., VIII. 1002.

	Calculated for $Ca(C_6H_5O_3)_2 . 2H_2O$.	Found. I.	II.	III.	IV.
Ca	12.28	12.24	12.31		
H_2O	11.04			10.97	10.99

I. 0.2688 grm. salt dried at 110° gave 0.1254 grm. $CaSO_4$.
II. 0.3109 grm. salt dried at 110° gave 0.1452 grm. $CaSO_4$.

	Calculated for $Ca(C_6H_5O_3)_2$.	Found. I.	II.
Ca	13.79	13.72	13.74

In determining the solubility of the salt, the calcium was precipitated as oxalate and weighed as sulphate.

I. 6.8529 grm. of a solution saturated at 20°.2 gave 0.4104 grm. $CaSO_4$.
II. 7.8851 grm. of a solution saturated at 20°.2 gave 0.4688 grm. $CaSO_4$.

I.	II.
12.77	12.68

Argentic Methylpyromucate, $AgC_6H_5O_3$. — This salt may readily be made by precipitation of a soluble salt with silver nitrate, and may be recrystallized from hot water. It is sparingly soluble even in boiling water, and crystallizes from aqueous solution in fine slender needles.

I. 0.2110 grm. salt gave on ignition 0.0977 grm. Ag.
II. 0.4007 grm. salt gave on ignition 0.1855 grm. Ag.

	Calculated for $AgC_6H_5O_3$.	Found. I.	II.
Ag	46.34	46.30	46.29

Sodic Methylpyromucate, $NaC_6H_5O_3$. — The sodium salt is exceedingly soluble even in cold water. It separated from its solution in dilute alcohol after long standing in compact clusters of small anhydrous needles.

I. 0.2752 grm. air-dried salt gave 0.1325 grm. Na_2SO_4.
II. 0.4240 grm. air-dried salt gave 0.2034 grm. Na_2SO_4.

	Calculated for $NaC_6H_5O_3$.	Found. I.	II.
Na	15.53	15.60	15.53

Potassic Methylpyromucate, $KC_6H_5O_3$. — The potassium salt is also very readily soluble in cold water, and crystallizes in spherical aggregations of short prisms, which appear to be anhydrous.

0.3385 grm. air-dried salt gave 0.1790 grm. K_2SO_4.

	Calculated for $KC_6H_5O_3$.	Found.
K	23.83	23.74

Ethyl Methylpyromucate, $C_6H_5O_3C_2H_5$. — The ethyl ether of the acid we made in the ordinary way by saturating a solution in an equal weight of absolute alcohol with hydrochloric acid. The excess of hydrochloric acid was then driven off at a gentle heat, the ether precipitated with water, washed with a dilute solution of sodic carbonate, dried with calcic chloride and distilled. The whole product passed over between 212° and 215°, and by far the greater portion showed the constant boiling point 213–214° with the mercury column completely in vapor under a pressure of 766 mm. The ether showed no tendency toward crystallization when cooled with ice and salt.

I. 0.2363 grm. substance gave 0.5404 grm. CO_2 and 0.1392 grm. H_2O.

II. 0.1570 grm. substance gave 0.3585 grm. CO_2 and 0.0921 grm. H_2O.

	Calculated for $C_6H_5O_3C_2H_5$.	Found.	
		I.	II.
C	62.34	62.36	62.27
H	6.49	6.54	6.52

Methylpyromucamide, $C_6H_5O_2NH_2$. — Ethyl methylpyromucate is readily attacked by concentrated aqueous ammonia, and the reaction is completed in the cold after the lapse of two days. The clear solution then yields on evaporation the corresponding amide in long colorless prisms which melt at 131°. It is readily soluble in alcohol, dissolves freely in hot benzol or ligroin, sparingly in the cold, and may best be recrystallized from hot water, in which it is readily soluble.

I. 0.2207 grm. substance gave 22.8 c.c. of moist nitrogen at 28° and under a pressure of 762 mm.

II. 0.1839 grm. substance gave 19.1 c.c. of moist nitrogen at 26° and under a pressure of 751 mm.

	Calculated for $C_6H_5O_2NH_2$.	Found.	
		I.	II.
N	11.20	11.36	11.38

Action of Bromine and Water.

Although Maquenne[*] had shown that the ready formation of methylfurfurol from isodulcite led directly to the conclusion that it must contain its methyl group in the δ position, it seemed desirable to establish this point by independent facts. Since pyromucic acid could readily be oxidized by bromine in aqueous solution, and converted into well marked bodies of the maleic acid group, it seemed probable that methylpyromucic acid would also yield analogous products. It was soon found that homogeneous products could not easily be obtained by using an excess of bromine, as is the case with pyromucic acid. Although a crystalline derivative could be obtained under certain conditions, the yield was not satisfactory, and viscous products were also formed. With two molecules of bromine, however, it was easy to reach definite results. Limpricht[†] showed in 1873 that pyromucic acid could be converted into a body which he called the half-aldehyde of fumaric acid by the action of two molecules of bromine upon its aqueous solution, and v. Baeyer[‡] subsequently proved that fumaric acid could be formed from this by the action of argentic oxide. It was evident, if methylpyromucic acid was decomposed in an analogous fashion, that there should be formed either an homologous aldehyde acid, or a ketone acid, according to the position of the methyl group in the furfuran ring. The formation of a ketone aldehyde under these conditions did not seem possible, since Hill and Sanger[§] had shown that the aldehyde group in analogous reactions is invariably formed from the δ carbon of the pyromucic acid. The product formed from methylpyromucic acid under these conditions proved to be a ketone acid, and a brief description of the results of a preliminary examination which was undertaken at the time by Mr. W. S. Hendrixson[||] and one of us was published elsewhere about two years ago. For the sake of completeness an account of these preliminary experiments will be included in the description of our own work, and we also owe to Mr. Hendrixson the analytical data which we publish. If methylpyromucic acid is suspended in about fifteen times its weight of cold water, and the vapor of bromine is slowly passed in by means of a current of air, the color of the bromine is quickly discharged, and the acid goes into solution with the escape of carbonic dioxide. When exactly two molecules of bromine have been added, the whole is allowed to stand for a short time, and the colorless solution then thoroughly extracted with ether. The ether left upon evaporation a crystalline body which was recrystallized from boiling benzol, and finally from water. An analysis showed that the formula of the substance was $C_5H_6O_3$.

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[*] Comptes Rendus, CIX. 603.

[†] Ann. der Chem. u. Pharm., CLXV. 285.

[‡] Berichte der deutsch. chem. Gesellsch., X. 1362.

[§] These Proceedings, XXI. 185.

[||] Berichte der deutsch. chem. Gesellsch., XXIII. 452.

0.2461 grm. substance gave 0.4734 grm. CO_2 and 0.1185 grm. H_2O.

	Calculated for $C_5H_6O_3$.	Found.
C	52.64	52.47
H	5.26	5.35

The new body was readily soluble in hot water, more sparingly soluble in cold water, and was acid in its character. It dissolved readily in alcohol, ether, or boiling chloroform, more sparingly in cold chloroform. In hot benzol it was quite readily soluble, and very sparingly soluble in cold benzol, carbonic disulphide, or ligroin. It crystallized in long slender lustrous needles, which melted at 122–123°. Recrystallization from various solvents failed to raise the melting point, but after several careful sublimations it melted at 123–124°. The formula of this acid was further controlled by an analysis of its silver salt, which was prepared by the cautious addition of ammonic hydrate to a solution of the acid containing argentic nitrate. The salt can be recrystallized from boiling water without difficulty, and forms concentrically clustered six-sided plates.

I. 0.2237 grm. salt gave 0.1901 grm. AgBr.
II. 0.2926 grm. salt gave 0.2484 grm. AgBr.

	Calculated for $AgC_5H_5O_3$	Found.	
		I.	II.
Ag	48.87	48.81	48.76

The acid which had thus been formed from methylpyromucic acid corresponded well with the description of the acetacrylic acid which Wolff[*] had shortly before made through the decomposition of β-bromlaevulinic acid. Its melting point, however, was given by Wolff as 125–125°.5, although he adds in a more recent paper* that impurities otherwise imperceptible may depress the melting point from two to three degrees. In order to compare the two acids, we have ourselves made the acetacrylic acid of Wolff from β-bromlaevulinic acid. In the preparation of the β-bromlaevulinic acid we followed with precision the directions of Wolff. The complete purification of the crude acid was in our hands attended with great loss of time and material, and, even after repeated recrystallization from carbonic disulphide, we failed to raise the melting point above 58°, while Wolff gives 59° as the melting point of the pure acid. Under these circumstances, we did not attempt to prepare pure β-bromlaevulinic acid in larger quantity, but decomposed with sodic acetate in an acetic acid solution a preparation which melted at 55–56°. The acetacrylic acid which we thus obtained was to all appearance identical with that made from methylpyromucic acid. As was to be expected, its melting point was somewhat low, 121–123°, but after several recrystallizations from benzol melted at 123–124°. Wolff† describes the silver salt of his acid as stellate needles, while the silver salt of our acid crystallized in well formed six-sided plates. We convinced ourselves that the same six-sided plates were formed by the addition of argentic nitrate to a moderately concentrated solution of both acids, and that on recrystallization these plates frequently formed dendritic aggregations. These dendritic forms only were seen if an insufficiently purified acid was used. While it is very possible that the acids which we had in our hands were in neither case absolutely pure, we cannot doubt the identity of the material from the two sources.

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[*] Berichte der deutsch. chem. Gesellsch., XX. 426.

In order to identify still further our product with Wolff's acetacrylic acid, we dissolved it in chloroform and added at low temperature one molecule of bromine. The color of the bromine was discharged, and on evaporation a crystalline residue was obtained which melted after recrystallization from a mixture of benzol and carbonic disulphide at 107–108°. According to Wolff† the αβ-dibromlaevulinic acid melts at this point. With phenylhydrazine our product also readily gave the corresponding hydrazone, identical in every respect with the body described by Bender‡ and shortly afterward by Decker.* It crystallized in small yellow prisms, which melted at 156–157°, and dissolved in concentrated sulphuric acid with a red color. Analysis showed that it had the formula $C_{11}H_{12}N_2O_2$.

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* Ann. Chem. u. Pharm., CCLXIV. 245.

† Ibid., p. 248.

‡ Berichte der deutsch. chem. Gesellsch., XXI. 2494.

I. 0.2240 grm. substance gave 0.5299 grm. CO_2 and 0.1190 grm. H_2O.

II. 0.2173 grm. substance gave 26.6 c.c. of moist nitrogen at 23° and under a pressure of 752 mm.

	Calculated for $C_{11}H_{12}N_2O_2$.	Found. I.	Found. II.
C	64.71	64.52	
H	5.88	5.90	
N	13.73		13.64

Bromine in aqueous solution, therefore, converts methylpyromucic acid into acetacrylic acid according to the equation

$$C_6H_6O_3 + 2\,Br_2 + 2\,H_2O = C_5H_6O_3 + CO_2 + 4\,HBr.$$

The formation of this ketone acid from methylpyromucic acid, while pyromucic acid under the same conditions yields an aldehyde acid, shows conclusively that the methyl group of the methylpyromucic acid stands in the δ place.

Action of Concentrated Sulphuric Acid.

We have thought that it might be possible to bring additional evidence as to the structure of the methylpyromucic acid through an investigation of the sulphonic acid derived from it. A study of the sulphonic acids derived from pyromucic acid had already shown that δ-sulphonic acids were always formed by the action of fuming sulphuric acid, whenever the δ hydrogen had not already been otherwise replaced; when the δ hydrogen had been thus replaced, β-sulphonic acids were formed. Moreover it was very easy to distinguish between the two isomers in that bromine in aqueous solution instantly formed sulphuric acid from the δ-sulphonic acids, while the β-sulphonic acids were oxidized to products which retained the sulpho group. Methylpyromucic acid was added with careful cooling to three times its weight of fuming sulphuric acid, the whole allowed to stand for twenty-four hours, and the diluted solution then neutralized with baric carbonate as usual. The barium salt which was obtained by evaporating the filtered solution crystallized in long needles, which were frequently collected in globular aggregations. The salt was hardly more soluble in hot than in cold water, and could best be obtained by the evaporation of its cold aqueous solution *in vacuo* over sulphuric acid. In this respect it closely resembled the baric β-sulphopyromucate. An analysis showed that the salt was baric sulphomethylpyromucate, and that it contained five molecules of water of crystallization.

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* Berichte der deutsch. chem. Gesellsch., XXI. 2937.

I. 0.4798 grm. air-dried salt gave 0.2597 grm. $BaSO_4$.
II. 0.6678 grm. air-dried salt lost at 165° 0.1383 grm. H_2O.

	Calculated for $BaC_6H_4SO_6\ 5H_2O$.	Found. I.	Found. II.
Ba	31.78	31.83	
H_2O	20.87		20.71

0.5272 grm. salt dried at 165° gave 0.3598 grm. $BaSO_4$.

	Calculated for $Ba\ C_6H_4SO_6$.	Found.
Ba	40.17	40.13

Bromine water gave in an aqueous solution of the salt no precipitate even on boiling, but after this treatment with bromine, if baric hydrate was added to alkaline reaction a white flocculent precipitate, which closely resembled baric sulphofumarate, appeared. This behavior showed conclusively that the sulpho group had not entered the furfuran ring in the δ position, and the conclusion seems warranted that it had not done so only because the methyl group already occupied that place.

Brommethylpyromucic Acids.

Bromine acts readily upon methylpyromucic acid at ordinary temperatures, and substitution is so easily effected that the isolation of an addition product is a matter of considerable difficulty. The instability of the addition product renders it unsuitable for the preparation of substituted acids, and facilitates the formation of satisfactory products by direct substitution. The nature of the products thus formed is, however, largely dependent upon the temperature at which the reaction takes place. At low temperatures the bromine enters first the furfuran ring and afterwards the methyl group, while at higher temperatures the methyl group is first attacked, although substitution apparently takes place at the same time to a certain extent in the ring. The facts which we have here observed evidently correspond precisely with those so thoroughly established in the aromatic series. Moreover, those bodies which contain the halogen in the side-chain are extremely susceptible to double decomposition, and are even decomposed by heating for a short time with water. The halogen in the main ring, on the other hand, is held quite as persistently as that in the corresponding derivatives of pyromucic acid. The study of these bodies presented at first many difficulties, the solution of which cost us so much time and labor that we have been unable to carry our researches as far as we had hoped. Since one of us must now relinquish the work, we shall present the results we have obtained, although they are in many respects incomplete. Further researches upon the subject will be made in this Laboratory. We are especially sorry that we have been unable to determine with precision the place in which the bromine enters the furfuran ring; while we have obtained by oxidation of the brommethylpyromucic acid in question an acid which is doubtless a bromacetacrylic acid, we have not yet been able to establish its structure and thus make it available in determining the constitution of the brommethylpyromucic acid from which it is formed. There can be little doubt, however, that the bromine in this case enters the β position, as it does with pyromucic acid itself as soon as the δ hydrogen atom is replaced by bromine.

β(?)-BROMMETHYLPYROMUCIC ACID.

When dry bromine acts at ordinary temperatures upon methylpyromucic acid, hydrobromic acid is at once evolved, and brommethylpyromucic acid is formed. The reaction is most readily controlled by the use of a solvent, and we have found glacial acetic acid most convenient for the purpose. We have found it necessary to add decidedly more than one molecule of bromine, and the best results were obtained by using three atoms. The methylpyromucic acid is dissolved in one and a half times its weight of glacial acetic acid (99.5 per cent), and the necessary amount of bromine carefully added, taking care that the temperature does not rise above 17°. After standing for some time at ordinary temperatures, the greater part of the hydrobromic acid is expelled *in vacuo* over lime, the residue poured into water, and the acid extracted with ether. The crude acid left on the distillation of the ether we have found it most advantageous to convert into the sodium salt with alcoholic sodic hydrate. The sodium salt is easily collected upon a filter, and the acid is then reprecipitated from its aqueous solution after decolorization with bone-black. The acid may be further purified by several repetitions of the same process.

I. 0.2279 grm. substance gave 0.2935 grm. CO_2 and 0.0526 grm. H_2O.

II. 0.1147 grm. substance gave 0.1055 grm. AgBr.

	Calculated for $C_6H_5BrO_2$.	Found. I.	II.
C	35.12	35.13	
H	2.44	2.56	
Br	39.02		39.15

Brommethylpyromucic acid crystallizes in colorless branching needles, which melt at 150–151°. It is readily soluble in alcohol, ether, or chloroform, somewhat sparingly soluble in cold, more readily in hot benzol. In carbonic disulphide or ligroin it dissolves but sparingly even on boiling. It is somewhat sparingly soluble in hot water, and is deposited in clusters of branching needles as the solution cools. The solubility of the acid in water at ordinary temperatures we determined in the usual way. We neutralized with baric carbonate the solution of the acid, and determined as sulphate the barium which had been dissolved.

I. 17.598 grm. of a solution saturated at 21°.4 gave 0.0271 grm. $BaSO_2$.

II. 16.031 grm. of a solution saturated at 21°.4 gave 0.0264 grm. $BaSO_4$.

The aqueous solution saturated at 21°.4 therefore contained the following percentages of the acid: —

I.	II.
0.27	0.29

For the further characterization of the acid we also prepared certain of its salts.

Baric Brommethylpyromucate, $Ba(C_6H_4BrO_3)_2 . 4 H_2O$. — This salt may readily be made from a solution of the ammonium salt by precipitation. It is sparingly soluble in cold water, more readily soluble in hot water, and crystallizes from the hot aqueous solution on cooling in dendritic needles, which contain four molecules of water. The salt is permanent in the air, but effloresces rapidly over sulphuric acid.

I. 0.4478 grm. air-dried salt gave 0.1690 grm. $BaSO_4$.
II. 0.8747 grm. air-dried salt lost at 110° 0.1030 grm. H_2O.

	Calculated for $Ba(C_6H_4BrO_3)_2 . 4 H_2O$.	Found. I.	Found. II.
Ba	22.20	22.19	
H_2O	11.67		11.78

0.3664 grm. salt dried at 110° gave 0.1558 grm. $BaSO_4$.

	Calculated for $Ba(C_6H_4BrO_3)_2$.	Found.
Ba	25.14	25.00

The solubility of the salt in cold water was determined in the usual way.

I. 19.211 grm. of a solution saturated at 20°.2 gave 0.0518 grm. $BaSO_4$.
II. 19.984 grm. of a solution saturated at 20°.2 gave 0.0466 grm. $BaSO_4$.

The aqueous solution saturated at 20°.2 therefore contained the following percentages of the anhydrous salt: —

I.	II.
0.63	0.55

Calcic Brommethylpyromucate, $Ca(C_6H_4BrO_3)_2 . 3 H_2O$.—The calcium salt we prepared by precipitating with calcic chloride an ammoniacal solution of the acid. It crystallized from hot water in clusters of short needles which contained three molecules of water. The salt was permanent in the air, and lost but little in weight over sulphuric acid.

I. 0.2508 grm. air-dried salt gave 0.0680 grm. $CaSO_4$.
II. 0 5443 grm. air-dried salt lost at 110° 0.0584 grm. H_2O.

	Calculated for $Ca(C_6H_4BrO_3)_2 . 3 H_2O$.	Found. I.	Found. II.
Ca	7.97	7.98	
H_2O	10.76		10.73

0.2724 grm. salt dried at 110° gave 0.0584 grm. $CaSO_4$.

	Calculated for $Ca(C_6H_4BrO_3)_2$.	Found.
Ca	8.93	8.86

In determining the solubility of the salt the calcium was precipitated as oxalate, and converted into sulphate before weighing.

I. 15.373 grm. of a solution saturated at 20° gave 0.0189 grm. $CaSO_4$.

II. 13.879 grm. of a solution saturated at 20° gave 0.0170 grm. $CaSO_4$.

The aqueous solution saturated at 20° therefore contained the following percentages of the anhydrous salt: —

I.	II.
0.41	0.40

Argentic Brommethylpyromucate, $AgC_6H_4BrO_3$. — The silver salt crystallizes from hot water in spherical aggregations of dendritic needles.

0.0956 grm. salt gave 0.0574 grm. AgBr

	Calculated for $AgC_6H_4BrO_3$.	Found.
Ag	34.61	34.48

Potassic Brommethylpyromucate, $KC_6H_4BrO_3$. — This salt is very readily soluble even in cold water, and crystallizes on slow evaporation of its aqueous solution in small anhydrous needles.

0.2789 grm. salt gave 0.0993 grm. K_2SO_4.

	Calculated for $KC_6H_4BrO_3$.	Found.
K	16.08	15.99

Action of Bromine and Water.

The whole behavior of the brommethylpyromucic acid showed conclusively that its bromine atom was situated in the furfuran ring. Although the bromacetacrylic acids had not yet been made, one of which would doubtless be formed by the oxidation of this brommethylpyromucic acid, and we therefore could not hope to determine whether the bromine was in the β or in the γ position, we nevertheless thought it best to investigate the products of oxidation. Brommethylpyromucic acid was suspended in thirty times its weight of water, and somewhat more than two molecules of bromine then slowly passed in by means of a current of air. The acid was readily carried into solution, and at the same time a small amount of an insoluble substance was formed. The filtered solution was extracted with ether, and the ethereal extract dried with calcic chloride. The viscous residue which was left on the distillation of the ether gradually solidified on standing over sulphuric acid *in vacuo*. This body proved to be an acid, containing bromine, readily soluble in water, but crystallizing from benzol by evaporation in rosettes. The melting point of the recrystallized acid was found to be 61°. An analysis showed that the percentage of bromine contained in this acid agreed with that required by a bromacetacrylic acid.

0.1630 grm. substance gave 0.1594 grm. AgBr.

	Calculated for $C_5H_5BrO_3$.	Found.
Br	41.45	41.62

The oxidation had therefore taken precisely the same direction as that followed by the analogous decomposition of methylpyromucic acid, and through this product of oxidation it will doubtless be possible at some future time to fix the constitution of the brommethylpyromucic acid. A product apparently identical with this we have also obtained by the action of dilute nitric acid.

The insoluble product formed at the same time with the bromacetacrylic acid we unfortunately have not been able to study further. It is not acid in its character, contains a large amount of bromine, and crystallizes from benzol in long colorless prisms, which melt at 90–91°.

ω-Brommethylpyromucic Acid.

Although bromine in acting upon methylpyromucic acid at ordinary temperatures enters at once the furfuran ring, at the temperature of boiling carbonic disulphide or chloroform it attacks chiefly the methyl group, and a bromine derivative is formed in considerable quantity which differs wholly in its properties from the acid just described. The reaction is not perfectly simple, for we have found that we could obtain the best yield of the new product by using twice the theoretical quantity of bromine. We have dissolved the methylpyromucic acid in six times its weight of chloroform and slowly added to the boiling solution two molecules of bromine diluted with its own weight of chloroform. The evolution of hydrobromic acid at once begins, and frequently before the bromine is all added a heavy crystalline body separates from the hot solution. When the reaction is over, the chloroform is well cooled, the crystalline product, which amounts to about sixty per cent of the weight of methylpyromucic acid taken, filtered off, and washed with cold chloroform. It may then be recrystallized from boiling chloroform or benzol.

I. 0.2152 grm. substance gave 0.2758 grm. CO_2 and 0.0490 grm. H_2O.

II. 0.1176 grm. substance gave 0.1079 grm. AgBr.

	Calculated for $C_6H_5BrO_3$.	Found. I.	Found. II.
C	35.12	34.95	
H	2.44	2.53	
Br	39.02		39.04

The ω-brommethylpyromucic acid crystallizes in small clustered oblique plates which melt at 147–148°. It is readily soluble in alcohol, ether, glacial acetic acid, or acetone, somewhat sparingly soluble in boiling benzol or chloroform, from which solvents it crystallizes well on cooling. In boiling toluol it is freely soluble, sparingly soluble in the cold, and almost insoluble in carbonic disulphide. It is but slowly acted on by cold water, but on warming it is readily dissolved with decomposition. The solution contains hydrobromic acid in abundance, and upon evaporation a crystalline acid is obtained, which is free from bromine. This behavior, which is in such striking contrast with the extreme stability of the derivatives of pyromucic acid that contain halogen, sufficiently establishes the position of the bromine in the side-chain. It also effectually prevented the preparation of its salts by the ordinary methods.

Decomposition by Water.

The product formed by the action of water upon ω-brommethylpyromucic acid we have studied a little more in detail. After heating an aqueous solution for some time at 100° it was evaporated over lime *in vacuo*. The hard black crystalline residue was dissolved in hot water, filtered from the separated carbon, and again evaporated. The brownish vitreous crystalline mass thus obtained melted with decomposition at 158–162°, and by recrystallization from a mixture of toluol and absolute alcohol the melting point could be raised to 162–163°, although the body still melted with decomposition. A combustion showed that the substance was ω-oxymethylpyromucic acid.

0.2623 grm. substance gave 0.4870 grm. CO_2 and 0.1052 grm. H_2O.

	Calculated for $C_6H_6O_4$.	Found.
C	50.70	50.63
H	4.23	4.46

ω-Oxymethylpyromucic acid is readily soluble in water, alcohol, or glacial acetic acid. In ether it is but slightly soluble, and in benzol, toluol, chloroform, or carbonic disulphide it is almost wholly insoluble. The barium salt of the acid is readily soluble in water, and is left as a varnish as its aqueous solution evaporates. From concentrated solutions it is thrown down as a flocculent precipitate on the addition of alcohol. We have not yet examined it further, and we have as yet found no other salts of a more inviting character.

The ease with which the ω-brommethylpyromucic acid entered into reaction with water naturally suggested the study of its behavior with other reagents. Unfortunately, we were unable to pursue our investigations in this direction, but further researches will be made in this Laboratory.

In the preparation of the ω-brommethylpyromucic acid small quantities of the isomeric acid were also apparently formed. From the chloroform mother liquors we obtained, after treatment with water and baric carbonate, a small amount of a crystalline acid which melted at 149–151°, and in other respects resembled the brommethylpyromucic acid first described.

ωβ(?)-Dibrommethylpyromucic Acid.

If the brommethylpyromucic acid melting at 150–151° is treated with bromine in boiling chloroform, a second atom of bromine enters the side-chain and a dibrommethylpyromucic acid is formed. The acid which separates on cooling or after partial evaporation of the solvent is washed with cold chloroform, and recrystallized from boiling toluol. This acid may perhaps more economically be made by the direct action of bromine at ordinary temperatures. Methylpyromucic acid is exposed over night to the vapor of three times its weight of bromine. The semiliquid product is well washed with carbonic disulphide, next with chloroform, and the dry crystalline residue recrystallized from boiling toluol. Our analyses are not altogether satisfactory, but they leave no doubt as to the nature of the body.

I. 0.2877 grm. substance gave 0.2735 grm. CO_2 and 0.0418 grm. H_2O.

II. 0.2086 grm. substance gave 0.2748 grm. AgBr.

	Calculated for $C_6H_4Br_2O_3$.	Found. I.	II.
C	25.35	25.92	
H	1.41	1.61	
Br	56.33		56.07

This dibrommethylpyromucic acid crystallizes in small oblique tabular crystals, which melt at 175° with decomposition. It is readily soluble in alcohol, ether, or glacial acetic acid, is but sparingly soluble in boiling benzol or chloroform, and almost insoluble in carbonic disulphide or ligroin. In boiling toluol it is quite readily soluble.

Action of Water.

On warming with water the acid is decomposed, hydrobromic acid is formed, and the solution then contains an oxybrommethylpyromucic acid. We prepared this acid first by treating with water the product formed by the vapors of bromine upon methylpyromucic acid, and separating it from the brommethylpyromucic acid melting at 151° which accompanied it by washing the mixed acids with benzol. The acid thus prepared from the crude material was absolutely identical with that afterwards made from the pure dibrommethylpyromucic acid. For analysis the substance was crystallized from a mixture of benzol and alcohol.

I. 0.1950 grm. substance gave 0.2333 grm. CO_2 and 0.0420 grm. H_2O.

II. 0.1695 grm. substance gave 0.1445 grm. AgBr.

	Calculated for $C_6H_5BrO_4$.	Found.	
		I.	II.
C	32.58	32.63	
H	2.26	2.39	
Br	36.20		36.28

The ω-oxy-β(?)-brommethylpyromucic acid is readily soluble in alcohol and ether, very sparingly soluble in boiling carbonic disulphide, somewhat more readily soluble in boiling chloroform, from which it separates on cooling in obliquely terminated prisms. It is sparingly soluble in hot benzol, and almost insoluble in ligroin. It is readily soluble in hot water, more sparingly in cold, and separates from dilute aqueous solutions in large obliquely terminated prisms, which contain one molecule of water. The crystals effloresce slowly over sulphuric acid, or even in the air after months of exposure, but we were unable to dehydrate them by heat without bringing about slight decomposition.

I. 0.4413 grm. of acid crystallized from water lost over sulphuric acid 0.0328 grm. H_2O.

II. 0.2117 grm. of acid dried in desiccator over night gave 0.1681 grm. AgBr.

	Calculated for $C_6H_5BrO_4 . H_2O$.	Found. I.	Found. II.
H_2O	7.53	7.43	
Br	33.47		33.80

The anhydrous acid melts at 153–154°, and on cooling forms a viscous gummy mass. Sodium amalgam reduces the acid without difficulty, and yields the ω-oxymethylpyromucic acid already described. The barium salt of the acid is readily soluble in water, and crystallizes in clustered short needles, but we have made no further study of its salts.

METHYLPYROMUCIC TETRABROMIDE.

We have already spoken of the instability of the addition product which methylpyromucic acid forms with bromine. We succeeded in isolating it by adding two molecules of bromine diluted with a little chloroform to a solution of methylpyromucic acid in five times its weight of chloroform well cooled with ice and salt. The bromine was slowly added with constant shaking, and at this low temperature but little hydrobromic acid was noticed. The addition product soon began to separate in flat colorless needles, which were frequently twinned at right angles. After the bromine had all been added, the whole was allowed to stand for a short time, and the product then quickly filtered upon the pump and washed with cold chloroform. It was then pressed with filter paper and dried in desiccator. As we found it impossible to recrystallize the substance without serious decomposition, we analyzed it without further purification. On exposure to moist air it rapidly liquefied, and even over sulphuric acid it soon evolved hydrobromic acid in abundance. Analyses IV. and V., made with material which had stood for two and four days respectively in desiccator, show how rapidly the decomposition progresses.

I. 0.2695 grm. substance gave 0.1668 grm. CO_2 and 0.0383 grm. H_2O.
II. 0.3509 grm. substance gave 0.2182 grm. CO_2 and 0.0467 grm. H_2O.
III. 0.2011 grm. substance freshly made gave 0.3393 grm. AgBr.
IV. 0.1564 grm. of same substance after two days gave 0.2601 grm. AgBr.
V. 0.1520 grm. of same substance after four days gave 0.2513 grm. AgBr.

	Calculated for $C_6H_6Br_4O_3$.	Found.				
		I.	II.	III.	IV.	V.
C	16.14	16.88	16.96			
H	1.35	1.58	1.48			
Br	71.74			71.81	70.79	70.37

Methylpyromucic tetrabromide is very sparingly soluble in carbonic disulphide or ligroin, somewhat less sparingly soluble in chloroform or benzol. In hot chloroform or benzol it dissolves more freely, but decomposition evidently ensues, for little unaltered substance crystallizes on cooling. The substance melts at about 95° with decomposition, but the melting point varies with the rapidity with which it is heated. Although the addition product is so unstable we have been able to find but few definite products resulting from its decomposition. Alcoholic sodic hydrate apparently destroys it completely. Sodic acetate in glacial acetic acid gives the brommethylpyromucic acid melting at 150–151°, and the same acid also appears to be formed in the spontaneous decomposition of the body when exposed to the air.

Further investigations in this direction will be made in this Laboratory.